



# Performance of carbon material derived from starch mixed with flame retardant as electrochemical capacitor



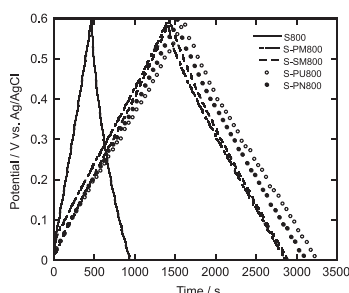
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## HIGHLIGHTS

- The properties of carbon derived from starch with an added flame retardant were investigated.
- The capacitance values were improved by the addition of the flame retardants.
- The N atoms derived from the flame retardants were incorporated in the synthesized carbon material.
- The P atoms or the S atoms were possibly incorporated in the synthesized carbon material.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Carbon materials derived from starch with an added flame retardant, such as melamine polyphosphate, melamine sulfate, guanidurea phosphate, or guanidine phosphate, were synthesized for investigating the performance as the electrode of an electrochemical capacitor. The yield after the heat treatment of the carbonization reaction increased by the addition of these flame retardants up to 800 °C. Although both the specific surface area and electrical resistivity are almost independent of the addition of the flame retardants, the capacitance values are improved with the addition of the flame retardants. The nitrogen atoms derived from the flame retardants are introduced to some extent into the synthesized carbon material. Moreover, the phosphorous atoms or the sulfur atoms derived from the flame retardants are doped into the synthesized carbon material. The method applied in this study, that is, the addition of flame retardants before the carbonization process can be used for the doping of the hetero atom such as N, P and S into the carbon material.

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## 1. Introduction

Many research studies have been performed for the development of carbon materials as the electrode of electrochemical capacitors such as the electrical double layer capacitor (EDLC) because the electrode is the most important component for the electrical storage [1–5]. Many ideas have been proposed for

improving the performance of the carbon material [1,6,7]. The addition of a hetero element, such as N, has been proposed as one of the approaches for improving the performance of the electrode for use in an electrochemical capacitor [8,9]. We have already reported that the addition of guanidine phosphate to starch before its heat treatment is effective for the improvement of the capacitive performance of the carbon material in an aqueous electrolyte [10,11]. It was confirmed that the N atom derived from the guanidine phosphate was incorporated to some extent into the synthesized carbon material. It is known that guanidine phosphate is one of the flame retardant for cellulose, which is a kind of

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polysaccharide like starch [12]. It is known that certain kinds of flame retardants for cellulose could be involved in the carbonization process of cellulose [12]. The chemical structure of starch is similar to that of cellulose. Therefore, these flame retardants are presumed to introduce the hetero atom to the carbon material derived from starch. Moreover, the chemical condition (chemical bond, networks of bonding, and so on) of the synthesized carbon material should be affected by the addition of the flame retardant, and the electrochemical property of the carbon material may be improved by the change its the chemical structure.

It is known that some reagents, such as melamine polyphosphate [13], melamine sulfate [14], and guanylurea phosphate [15], act as flame retardants. These flame retardants contain a hetero atom, such as N, P, and S, like guanidine phosphate. Therefore, it is presumed that these reagents would also be effective for improving the performance of the carbon material derived from starch for use in an electrochemical capacitor. Because the addition of a flame retardant before the heating process is simple, easy, safe, and inexpensive, this method should be important for practical use. Therefore, the investigation of the effect of the addition on the performance should be important for the development of a carbon material for use in an electrochemical capacitor. In this study, the effect of the addition of these reagents to starch on the performance of the electrode of an electrochemical capacitor was investigated in detail.

## 2. Experimental

Commercial starch (Starch, Soluble, Wako Pure Chemical Industries, Ltd.) was mixed with a flame retardant at the weight ratio of (starch:flame retardant) = 10:1. In this study, melamine polyphosphate, melamine sulfate, guanylurea phosphate, and guanidine phosphate were used as the flame retardant. The mixtures were heated at 700–900 °C for 1 h under flowing N<sub>2</sub> (50 mL min<sup>-1</sup>). The powders after the heat treatment were used for the measurements by the BET method (nova4200e, Quantachrome Instruments) and CHN-corder (CHN CORDER MT-5, Yanaco). The XPS measurements were performed for the analysis of the hetero atoms (N, P or S) derived from the flame retardants by using Shimadzu/KRATOS AXIS-NOVA. The peak of C 1s was used for the calibration as 284.6 eV. The powders prepared by the heat treatment, acetylene black, and Teflon powder were mixed at an 8:1:1 ratio to form sheets. The sheets were cut and then used as the sample for the measurement of the electrical resistivity and the electrode for the electrochemical measurements. The electrical resistivity was measured by the DC four-probe method. The sheets were placed in a three-electrode cell, and Pt plates were used as the counter electrode and collector electrode and a Ag/AgCl electrode was used as reference electrode. The capacitance values were calculated from the data for the charging process. In this study, starch, melamine polyphosphate, melamine sulfate, guanylurea phosphate, and guanidine phosphate were abbreviated S, PM, SM, PU, and PN, respectively. Moreover, the information about the treatment temperature was described on the label of the samples. In the case of the sample washed with water, “W” was used for the label. For example, when starch mixed with melamine polyphosphate was heated at 800 °C and the sample was washed with water, the label of the sample was S-PM800W.

## 3. Results and discussion

In order to estimate the yield of the sample, the weights were measured before and after the heat treatment. The yields, the value of  $100 \times (\text{the weight after the heat treatment})/(\text{the weight before the heat treatment})$ , are shown in Fig. 1. The yield of S700 was

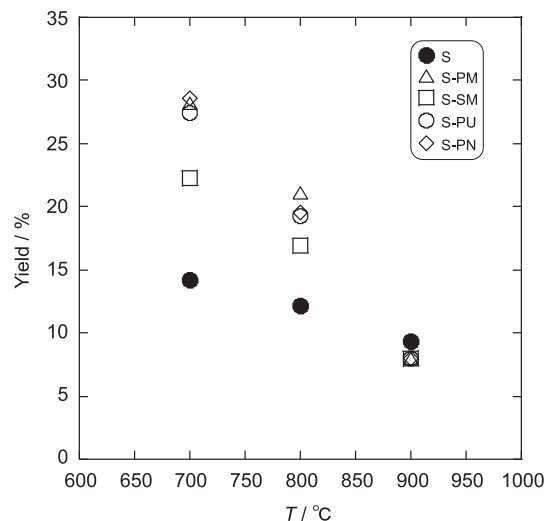


Fig. 1. Heating temperature dependence of yield.

14.2%. The yields decreased with the increasing heating temperature, and reached 9.3% at 900 °C. The yields of S-PM700, S-PU700, and S-PN700 were ca. 28%, and the yield of S-SM700 was 22.3%. When the heating temperature was less than 800 °C, the yields for the samples with the added flame retardants were greater than that for only the starch sample. On the other hand, when the heating temperature was 900 °C, the yields for the samples with the added flame retardants were slightly lower than those for only the starch sample. There was no effect of the flame retardants on the enhancement of the yield at 900 °C.

The CV graphs of the samples are shown in Fig. 2. The area of the CV curves for the samples derived from only starch was relatively small, which should mean that the capacitance values are lower than those of the other samples. Therefore, the addition of the flame retardants could enhance the capacitance values. Some CV curves of the samples, such as S-PU800, had broad peaks, which may be derived from the pseudocapacitance. All the CV graphs of the samples treated at 900 °C had a rectangular shape, which should mean that there was no pseudocapacitance.

The heating temperature dependence of the specific surface area is shown in Fig. 3. The specific surface area of all the samples increased with the increasing heating temperature. At 700 °C, the samples with added flame retardant except for S-SM had lower specific surface areas than the sample derived from only starch. On the other hand, at 900 °C, all the samples with the added flame retardant had higher specific surface areas than the sample derived from only starch. This result should be one of the facts that the flame retardants affected the carbonization process of the starch. However, the specific surface area values did not drastically change by the addition of the flame retardants. Some of the flame retardants used in this study were phosphates, which contain the phosphoric acid component. It is known that phosphoric acid acts as an activator for the synthesis of activated carbon. Although it might be postulated presume that the flame retardants used in this study act as the activator, the specific surface areas of the samples with the added flame retardants had values similar to that of the starch only sample. Liu et al. [16] reported that the specific surface area of the carbon material derived from a lotus stalk with added guanidine phosphate was much lower than that with added phosphoric acid when the heat treatment temperature was 450 °C. Therefore, these phosphates have a low activity as the activator for the synthesis of activated carbon.

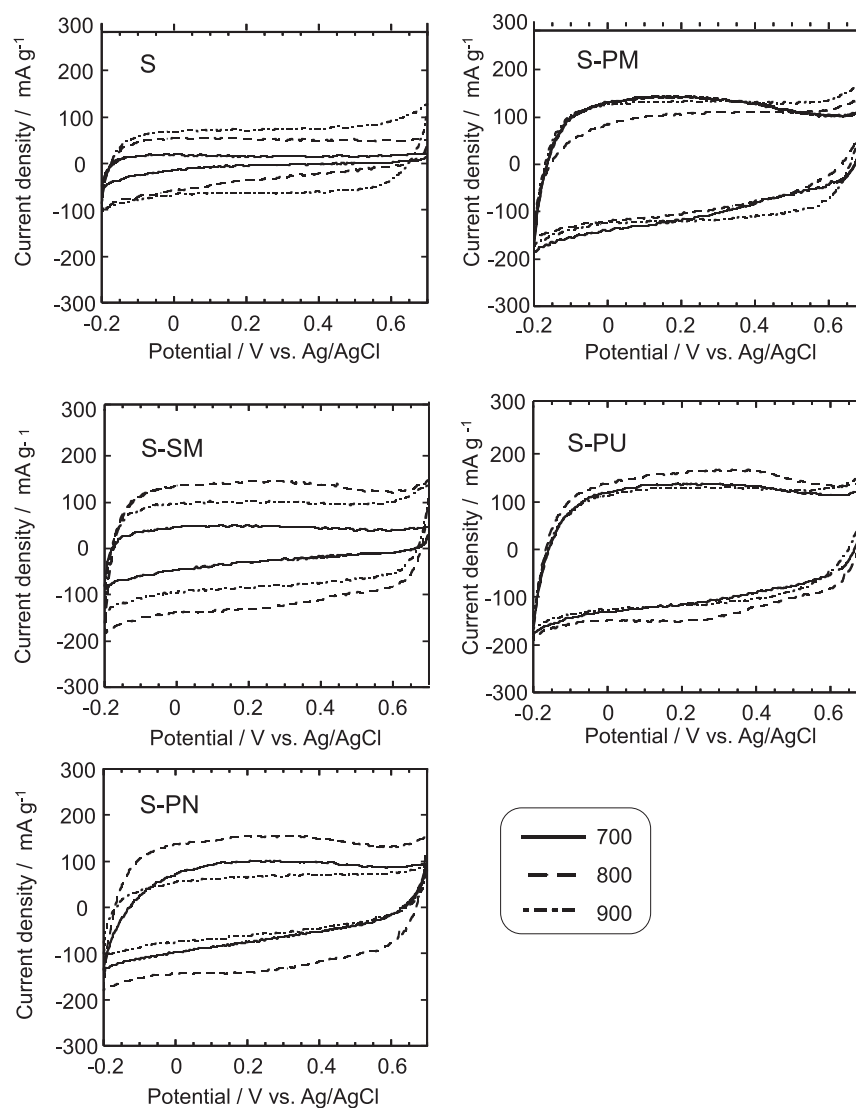


Fig. 2. CV graphs of the samples.

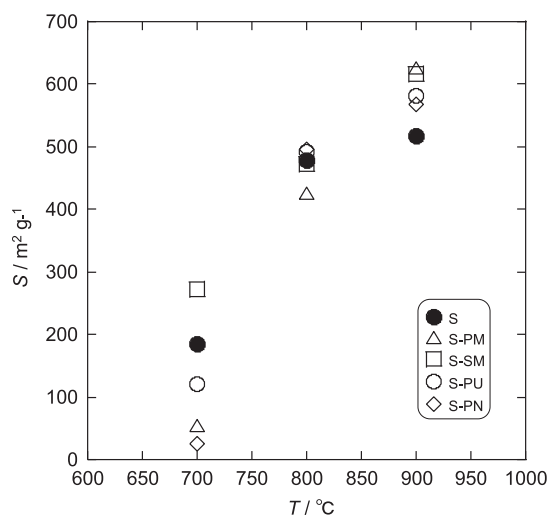


Fig. 3. Heating temperature dependence of specific surface area.

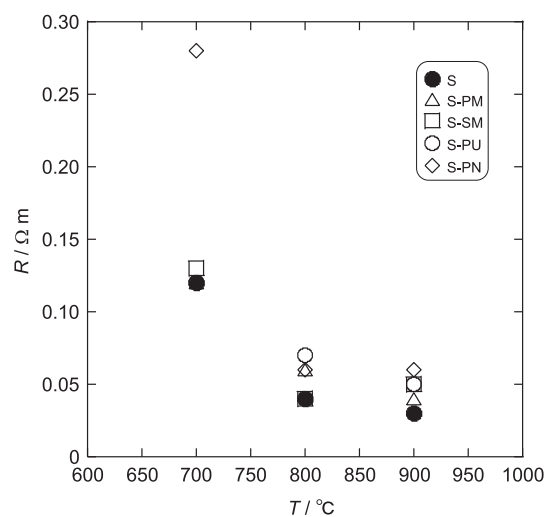


Fig. 4. Heating temperature dependence of electrical resistivity.

The heating temperature dependence of the electrical resistivity is shown in Fig. 4. The electrical resistivity decreased with the increasing heating temperature. The sample derived from only starch had the lowest values at all the temperatures. The heating temperature dependence of the nitrogen percent is shown in Fig. 5. The percentage of the N atom in the sample derived from only starch was almost zero because there is no nitrogen in the chemical structure of starch. (The reason for the low amount of the N atom in the sample of S-700 might be due to contamination.) The samples with these added flame retardants contained a few percent (2–5 wt.%) of the N atoms. Because the flame retardants contain nitrogen in their chemical structures, the N atoms should come from the flame retardants. As for all the samples with the added flame retardants, the percent of N decreased with the increasing temperature. The results of the CHN-corder are listed in Table S1 (supplementary material), and the percentages of the elements other than C, H, and N are shown in Fig. S1 (supplementary material). As shown in Fig. S1 (supplementary material), the percentage, which should consist of O and P (or S), were maximum at 800 °C. The values of “others” for the added samples except for S-SM were higher than that for the sample derived from only starch. The values of “others” should contain the percents of oxygen and phosphorous (or sulfur in the case of S-SM). Therefore, it should be presumed that the excessive values of “others” are for the percent of phosphorous (or sulfur in the case of S-SM). The high values for all the samples with the added flame retardants containing phosphorous were ca. 10 wt.%. On the other hand, the S-SM samples had an “others” value similar to the samples of only starch. The use of the flame retardant could be important for the doping of two kinds of hetero atoms into the carbon material.

The graphs of the experimental results from the charge–discharge test at 50 mA g<sup>−1</sup> are shown in Fig. 6. The shapes of the graphs were triangles, which should mean that these samples acted as capacitors. The capacitance values from the charge process were calculated from the charge–discharge test data. The heating temperature dependence of the capacitance value during the charge process of 50 mA g<sup>−1</sup> is shown in Fig. 7. The capacitance value of the sample derived from only starch increased with the increasing heating temperature although the values were the lowest of all the samples. All the samples with these added flame retardants had larger capacitance values than that derived from only starch, and had the maximum capacitance values at 800 °C. Moreover, the capacitance values were larger than that of a commercial activated carbon. The used activated carbon was not

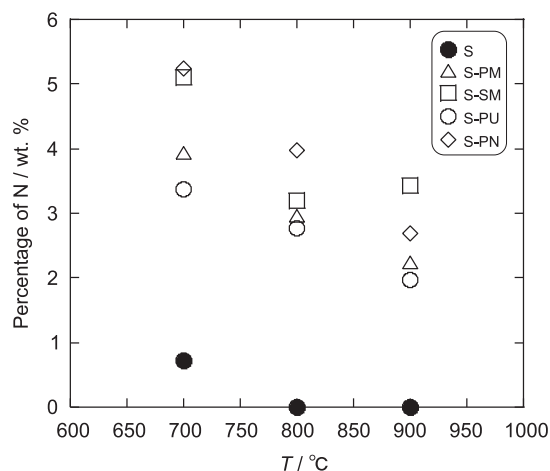


Fig. 5. Heating temperature dependence of the nitrogen percentage.

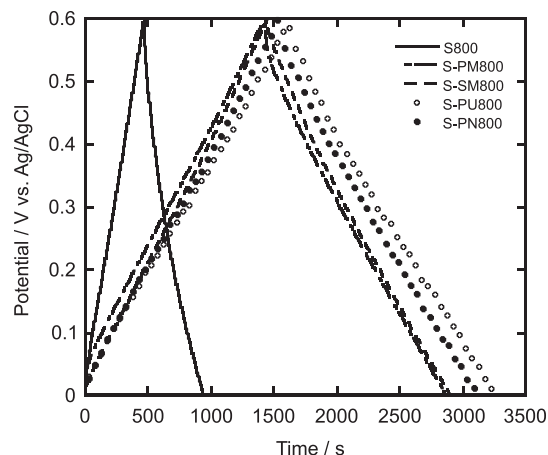


Fig. 6. Experimental results of charge–discharge test (50 mA g<sup>−1</sup>).

industrial material for EDLC but reagent for research work. Therefore, the absolute value of the capacitance may not be meaningful for the judgment of the practical use. However, the comparable performance to activated carbon should be valuable because the samples were prepared without activation process. The capacitance value of S-PU800, which was ca. 137.62 F g<sup>−1</sup>, was the highest of all the capacitance values. However, the capacitances for the samples with these added flame retardants were similar to each other. Therefore, these flame retardants should have a similar ability for improving the capacitance performance of the carbon material derived from starch.

It could be presumed that if the residue derived from the flame retardants dissolved in the electrolyte solvent is ion species, the capacitance values might be affected by these ion species. Therefore, in order to remove the residue, which can dissolve in water, the washing treatment with water was repeatedly performed. The effect of the washing process on the percentage of nitrogen, specific surface area, the electrical resistivity, and the capacitance values during the charge process of 50 mA g<sup>−1</sup> are shown in Fig. 8. The percentages of the elements other than C, H, and N, before and after

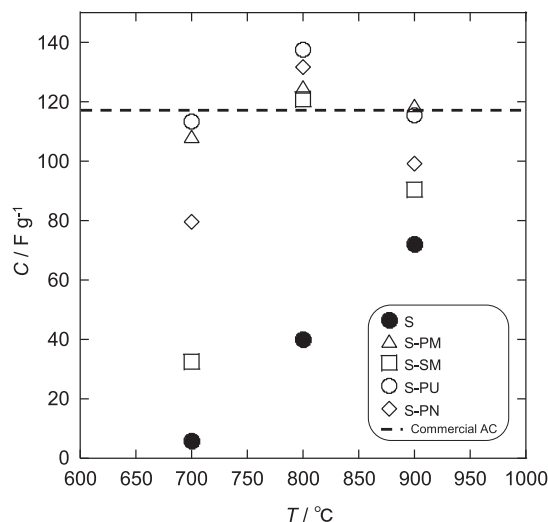
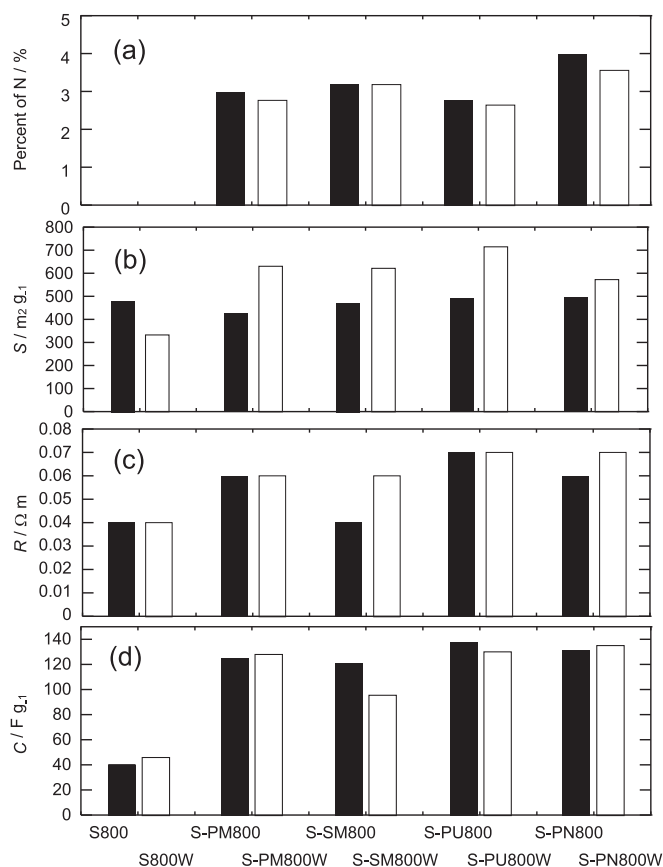


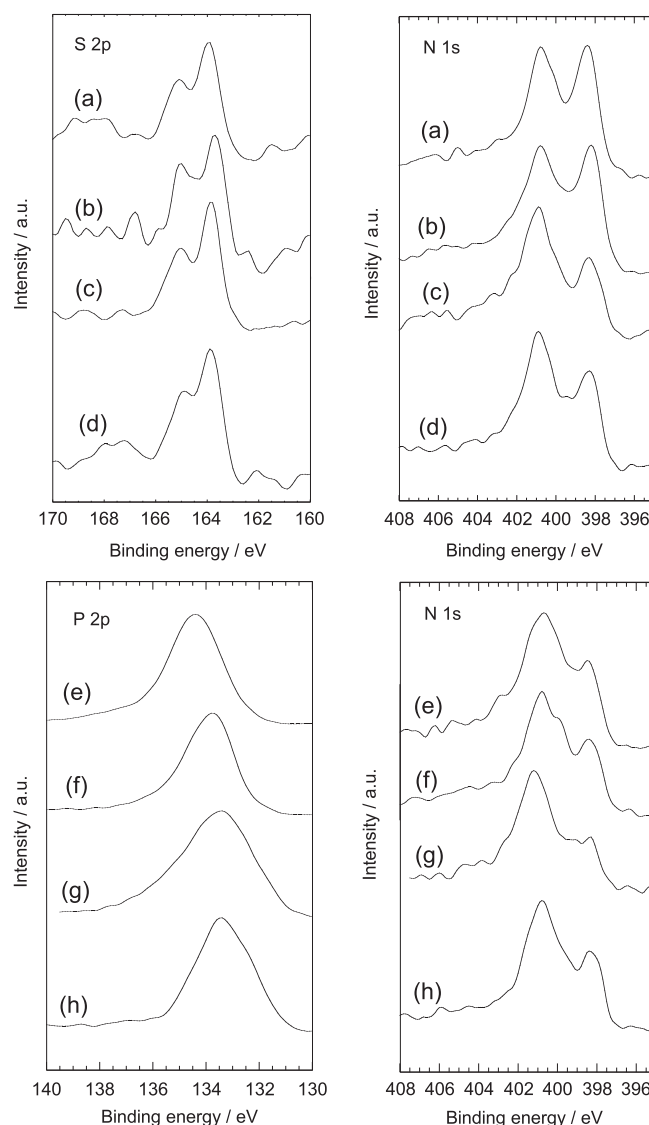
Fig. 7. Heating temperature dependence of capacitance value (charge process: 50 mA g<sup>−1</sup>).



**Fig. 8.** Effect of the washing process. (a) Percentage of nitrogen, (b) specific surface area, (c) electrical resistivity, (d) capacitance values (1 M  $H_2SO_4$  aq., 50 mA  $g^{-1}$ ).

the washing process are shown in Fig. S2 (supplementary material). The specific surface of the samples increased with the washing process, except for S800. The percentage for all the samples except for S-SM800 decreased with the washing process. On the other hand, that for S-SM800 increased with the washing process. The reason for the changes in the specific surface areas could be the removal of the residue in the pores on the sample surface. For S800, the decrease in the specific surface area might be caused by the removal of the small particles which have a high specific surface area. The percentages of nitrogen in the samples were unchanged by the washing process. Therefore, the N atoms should be stable in water. Therefore, the N atoms could exist not as nitrate salt, but as a functional group or structure of the carbon material. The values of the electrical resistivity were independent of the washing treatment, except for S-SM800. The CV graphs of the samples are shown in Fig. S3 (supplementary material). The graphs after the washing process were almost the same as those before the washing process, except for S-SM800. Therefore, the sample conditions should be unchanged by the washing process, except for S-SM800. It could be presumed that the P atoms were also introduced into the carbon materials. Although the specific surface area of the samples with the added flame retardants increased with the washing process, the capacitance values were not affected, except for S-SM800. The reason for the unchanged capacitance values is unclear. However, it is obvious that the addition of the flame retardants is effective for enhancing the capacitance value.

In order to analyze the hetero atoms derived from the flame retardant, the XPS spectra for the samples of S-SM and S-PM are shown in Fig. 9. The samples of S-SM had the peaks assigned to S



**Fig. 9.** XPS spectra for the samples. (a) S-SM700, (b) S-SM800, (c) S-SM900, (d) S-SM800W, (e) S-PM700, (f) S-PM800, (g) S-PM900, (h) S-PM800W.

and those assigned to N even though the sample after the washing process, and the peak positions were independent of the heating temperature. However, the relative intensity of the peak at ca. 398 eV, which could be assigned to pyridinic N [17], decreased with the washing process. The removal of the residue containing pyridinic structure could be the reason for the increment of the specific surface area and increment of the percentage of other than C, H, and N. The samples of S-PM also had the peaks assigned to P and those assigned to N even though the sample after the washing process. Moreover, the relative intensities of the peaks assigned to the N atoms were independent of the washing process. The peaks assigned to the N atoms for these samples except S-SM700 and S-SM800 were similar to the sample prepared from starch added guanidine phosphate [11]. Therefore, the condition of the N atom introduced in the carbon material could be presumed to be independent of the kind of the flame retardant. The binding energy of the P atom for the samples of S-PM seemed to decrease with increasing the heating temperature, that is, the P atoms in S-PM were slightly reduced at high temperature. On the other hand, the

peak positions of the S atoms for the samples of S-SM, which could be assigned to  $S^0$ , were independent of the heating temperature in this study, and the peak positions were similar to those of the carbon derived thiourea-formaldehyde resin [18]. Zhao et al. reported that 4,4'-thioldiphenol derived mesoporous carbon had superior capacitance, and they presumed that the enlarged polarization with S-doping in aromatic structure is one of the effects for the enhancement of capacitance [19]. One of the reasons for the larger capacitance value of S-SM than S could be the enlarged polarization with S-doping. Wang et al. reported the capacitance of phosphorous- and nitrogen-co-doped carbon derived from glucose [20]. They concluded that synergetic effect of pseudocapacitance derived from the functional groups and the electrical double layer capacitance derived from the micropores developed by *in situ* activation with ammonium phosphate. There was no data about the amount of micropores for the samples of this study. However, the effect of the addition of the flame retardant on the specific surface area was not large as shown in Fig. 3. Therefore, the introduction of micropores should not be main reason for the improvement of the capacitance value in this study.

#### 4. Conclusions

The capacitance performance in an aqueous electrolyte was investigated for carbon materials derived from starch mixed with a flame retardant such as melamine polyphosphate, melamine sulfate, guanidylurea phosphate, and guanidine phosphate. The XPS data indicated that nitrogen was incorporated to some extent with the addition of these flame retardants, and that the phosphorous (or sulfur) was also introduced into the carbon material. Therefore, the flame retardant could dope two kinds of hetero atoms into the carbon material. Although the addition of the flame retardants was ineffective for changing the specific surface area, the capacitance values typically increased with the addition of the flame retardants. The addition of a reagent, which has a flame-retardant effect,

should be one of the approaches for controlling the property of the carbon material.

#### Appendix A. Supplemental material

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.05.140>.

#### References

- [1] M. Inagakia, H. Konno, O. Tanaikab, J. Power Sources 195 (2010) 7880–7903.
- [2] N.S.A. Manaf, M.S.A. Bistamam, M.A. Azam, ECS J. Solid State Sci. Technol. 2 (10) (2013) M3101–M3119.
- [3] X. Lia, B. Weia, Nano Energy 2 (2013) 159–173.
- [4] M. Noked, A. Soffer, D. Aurbach, J. Solid State Electrochem. 15 (2011) 1563–1578.
- [5] A.K. Shukla, A. Banerjee, M.K. Ravikumar, A. Jalajakshi, Electrochim. Acta 84 (2012) 165–173.
- [6] H. Nishihara, T. Kyotani, Adv. Mater. 24 (2012) 4473–4498.
- [7] P. Simon, Y. Gogotsi, Acc. Chem. Res. 46 (2013) 1094–1103.
- [8] L. Sun, C. Tian, Y. Fu, Y. Yang, J. Yin, L. Wang, H. Fu, Chemistry-A Eur. J. 20 (2014) 564–574.
- [9] L. Sun, C. Wang, Y. Zhou, Q. Zhao, X. Zhang, J. Qiu, J. Solid State Electrochem. 18 (2014) 49–58.
- [10] T. Tsubota, T. Yamaguchi, C. Wang, Y. Miyauchi, N. Murakami, T. Ohno, J. Power Sources 227 (2013) 24–30.
- [11] T. Tsubota, Y. Miyauchi, N. Murakami, T. Ohno, J. Power Sources 196 (2011) 5769–5773.
- [12] A. Granzow, Acc. Chem. Res. 11 (1978) 177–183.
- [13] I. Veen, J. Boer, Chemosphere 88 (2012) 1119–1153.
- [14] P.J. Schmitz, J.W. Holubka, L.F. Xu, J. Coatings Technol. 72 (2000) 39–45.
- [15] S. Kikuchi, S. Maeda, Mokuzai Gakkaishi 53 (2007) 276–282.
- [16] H. Liu, Q. Gao, P. Dai, J. Zhang, C. Zhang, N. Bao, J. Anal. Appl. Pyrolysis 102 (2013) 7–15.
- [17] H. Konno, T. Ito, M. Ushiro, K. Fushimi, K. Azumi, J. Power Sources 195 (2010) 1739–1746.
- [18] T. Tsubota, K. Takenaka, N. Murakami, T. Ohno, J. Power Sources 196 (2011) 10455–10460.
- [19] X. Zhao, Q. Zhang, C.-M. Chen, B. Zhang, S. Reiche, A. Wang, T. Zhang, R. Schlögl, D.S. Su, Nano Energy 1 (2012) 624–630.
- [20] C. Wang, Y. Zhou, L. Sun, P. Wan, X. Zhang, J. Qiu, J. Power Sources 239 (2013) 81–88.